

Understanding Gold Plating

Peter Wilkinson

Engelhard Limited, Cinderford, Gloucestershire, United Kingdom

For effective operation, gold plating baths must require the minimum of attention in respect of replenishment and replacement, and must produce as little sub-standard or reject work as possible. To achieve this, an understanding of the processes involved and the factors affecting them is advantageous. This article attempts to provide such an understanding in a simple manner. Special attention is given to the plating of gold from acid baths containing monovalent gold complexes.

The use of gold as a contact material on connectors, switches and printed circuit boards (PCB's) is now well established. There is also an awareness that only gold deposits from acid (pH 3.5–5.0) gold(I) cyanide baths containing cobalt, nickel or iron as brightening agents have the appropriate properties for a contact material. Gold deposits from: pure gold(I) cyanide baths; from such baths containing organic materials as brightening agents; or from electrolytes containing gold in the form of the gold(I) sulphite complex, do not have the sliding wear resistance which is necessary for make and break connections (1).

It was known for many years that deposits from acid gold(I) cyanide baths brightened with cobalt, nickel or iron contained about 0.25 per cent of base metal, but this did not explain why their densities (16.0–17.0 g/cm³) were so much lower than the density of pure gold deposits (19.3 g/cm³). The classical experiment of Munier (2), in which she dissolved the gold of the brightened deposits in *aqua regia* vapour to reveal a polymer network, showed that deposits of this type were much more complex than was formerly thought.

In what follows, an earlier account (3) of the factors involved in the formulation and operation of acid gold plating baths is brought up to date. Brief accounts are also included of the electrodeposition of gold from gold(III) cyanide baths and from gold(I) sulphite baths.

The Formulation of Gold Electrolytes

Range of Electrolytes Available

There are only three complexes of gold which are suitable for commercial use in gold plating baths. By far the most important are the cyanide and sulphite complexes of gold(I), of which the potassium derivatives are $\text{KAu}(\text{CN})_2$ and $\text{K}_3\text{Au}(\text{SO}_3)_2$ respectively.

Other gold(I) complexes, such as those with thiomalate and thiosulphate have been considered, but it is doubtful if they will ever find commercial application.

In terms of electricity consumed, gold(I) baths are more efficient than gold(III) baths. Thus, assuming 100 per cent efficiency, 100 amp-min will deposit 12.25 g of gold from a monovalent gold complex, but only 4.07 g from a trivalent gold complex.

Nevertheless, deposition from acid gold(III) cyanide baths has merit in the plating of acid resistant substrates such as stainless steels, to which electrodeposited gold normally adheres badly because of their passivated surfaces. Hence, these baths can also be used to produce decorative gold alloy coatings on such substrates.

The Deposition Process

Figure 1 is a schematic diagram of what is thought to happen during the deposition of a metal from a solution of one of its complexes.

The cathode attracts predominantly positive ions to a region near its surface which is known as the Helmholtz double layer.

In addition, negatively charged complex ions, such as the $\text{Au}(\text{CN})_2^-$ ions present in the gold(I) cyanide plating baths, which approach this layer become polarised in the electric field of the cathode.

The distribution of the ligands around the metal is thereby distorted and the diffusion of the complex ion into the Helmholtz layer is assisted.

Finally, within the Helmholtz layer the complex breaks up. Its component ligand ions or molecules are freed and the metal released in the form of the positively charged metal cation which is deposited as the metal atom on the cathode.

It will be appreciated from this simple picture of events at the cathode, that the ease of gold deposition from gold(I) cyanide baths, which contain gold in the form of $\text{Au}(\text{CN})_2^-$ ions, will depend on the ease with which these ions dissociate into Au^+ and CN^- ions, thus:



The mass action law dictates that for a reversible reaction:

$$\frac{[\text{Au}(\text{CN})_2^-]}{[\text{Au}^+][\text{CN}^-]^2} = \text{a constant} \quad 2$$

where $[\text{Au}(\text{CN})_2^-]$, $[\text{Au}^+]$ and $[\text{CN}^-]$ are the concentrations of the respective ions in solution.

This constant (4) provides a measure of the stability of the $\text{Au}(\text{CN})_2^-$ complex and is referred to as its stability constant β_2 (the subscript 2 indicates that the reaction is two stage).

The value of β_2 for the $\text{Au}(\text{CN})_2^-$ ion has been determined as $10^{38.3}$. This is exceedingly large and implies that the equilibrium in reaction (1) is far to the left and that the $\text{Au}(\text{CN})_2^-$ ion is a very stable one. Moreover, it indicates that the concentration $[\text{Au}^+]$ of Au^+ ions is given by equation:

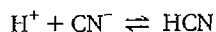
$$[\text{Au}^+] = \frac{[\text{Au}(\text{CN})_2^-]}{[\text{CN}^-]^2} \cdot 10^{-38.3}$$

This is an exceedingly low concentration and it would appear as if reasonable rates of deposition of gold from gold(I) cyanide solutions are possible only because of the polarisation of $\text{Au}(\text{CN})_2^-$ ions which approach the cathode surfaces and their decomposition in accord with equation 1 within the Helmholtz layer.

The electrodeposition of gold from its other complexes is thought to occur in a similar manner.

Gold(I) Cyanide Baths

These may be operated under alkaline, neutral or acid conditions. Under acid conditions, the value of $[\text{Au}^+]$ is increased as a result of the equilibrium reaction:



in which the formation of undissociated HCN is strongly favoured. Acid gold(I) plating baths are therefore characterised by low free cyanide ion concentrations. However, under alkaline conditions and especially if potassium cyanide is present, the value of $[\text{CN}^-]$ is greatly increased. Following equations 1 to 3 this means that in acid baths the value of $[\text{Au}^+]$ is increased,

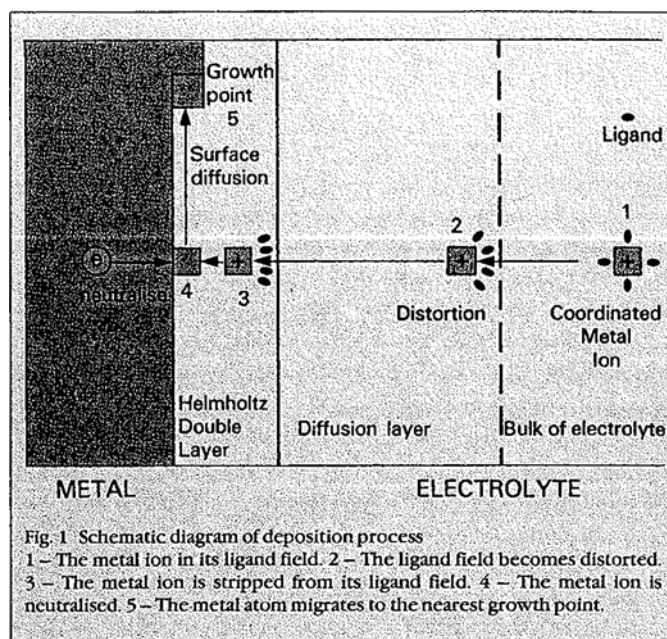
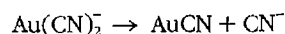


Fig. 1 Schematic diagram of deposition process
1 – The metal ion in its ligand field. 2 – The ligand field becomes distorted. 3 – The metal ion is stripped from its ligand field. 4 – The metal ion is neutralised. 5 – The metal atom migrates to the nearest growth point.

whereas in alkaline baths it is decreased. Despite the fact that the stability constant of the $\text{Au}(\text{CN})_2^-$ ion is unchanged, this complex ion therefore appears to be less stable in acid than in alkaline media. The range of usefulness of gold(I) cyanide baths in acid media is limited, however, by the tendency of the $\text{Au}(\text{CN})_2^-$ complex to decompose at pH's below about 3 with precipitation of AuCN thus:



Both polarographic and potentiometric studies have shown that the gold(III) cyanide complex $\text{Au}(\text{CN})_4^-$ is formed in acid gold(I) cyanide plating baths during operation, presumably by oxidation at the anode (5,6). It is important to realise that any gold oxidised to the trivalent state in this manner is not available for deposition at the cathode because gold(I) and hydrogen are preferentially deposited. The efficiency of the bath therefore falls, not because some gold is being deposited from gold(III) cyanide, but because the effective concentration of gold(I) cyanide in the bath has been reduced. Also gold(III) is just as susceptible to 'drag out' as the gold(I) and the metal's valency does not affect its price.

Modern acid gold(I) cyanide baths are therefore formulated with the addition of a mild reducing agent so as to minimise the formation of gold(III) cyanide, but baths formulated several years ago can give rise to gold(III) cyanide formation especially under unusual plating conditions, such as wire plating. Since the gold(III) complex is also very stable, it is better to prevent its formation than to reduce it back to gold(I) cyanide.

Gold(III) Cyanide Baths

As has been indicated above, acid gold(I) cyanide plating baths are normally operated at pH values between 3.5 and 5. They cannot be operated at pH values less than 3.5, since under such acid conditions the gold is precipitated as AuCN. Moreover, deposits from acid gold(I) cyanide baths have little ductility so that plated articles cannot be subsequently deformed without risk of cracks developing in the surface coating. These and other limitations of acid gold(I) cyanide baths have stimulated studies in recent years of the deposition of gold from gold(III) cyanide baths.

Thus, a method for the preparation of $\text{HAu}(\text{CN})_4$ and the formulation of gold plating baths based upon this gold complex were described in 1971 (7). The baths were found to have excellent plating characteristics at pH values from 0.1 to 5.0, and gave optimum performance in the pH range 1.0 to 3.0. They typically contained the gold complex, a citrate, phosphate or tartrate, a weak organic acid and a mineral acid such as phosphoric acid.

Then in 1979 the plating of gold strikes on stainless steel substrates using gold(III) cyanide baths was claimed (8). Potassium nitrate was used as the electrolyte in these baths and ethylenediamine hydrochloride as a complexant. Nickel, cobalt, copper, tin and indium could be incorporated as alloying constituents and the baths operated at pH's preferably less than 1.5.

The gold(III) cyanide complex was generated directly by warming a solution containing KAuCl_4 , KNO_3 and KCN , the pH of which was subsequently adjusted by additions of hydrochloric acid. This gave rise to evolution of chlorine at the anode and severe corrosion problems, so that significant exploitation of the patent did not follow, though the deposition of gold-tin alloy coatings from baths of this type has been claimed (9).

More recently (10-11), a study of the galvanic deposition of gold and gold alloys from baths based upon potassium gold(III) cyanide has resulted in the formulation of chloride-free baths which are finding limited application for special purposes. Not only are the deposits bright, hard and relatively free from non-metallic components, but they are also ductile and relatively pore-free. They have low contact resistance which is not affected by heat.

These properties can be modified by additions of alloying metals such as Co, Ni, In, Sn, Zn or Cd. Other components of the baths may include an amine, amino acid or phosphonic acid, with the pH being adjusted preferably to between 0.6 and 2.0 by the addition of phosphoric acid or sulphuric acid or mixtures of these, plus citric acid, phosphate and sulphate. Addition of chlorides to the baths was scrupulously avoided.

Other gold(III) cyanide baths (12,14) have also been developed recently.

It must be stressed, however, that these baths are not used commercially to any great extent. The deposits they yield cannot be used in contact applications in electronics because their wear resistance is inadequate against existing gold plated contacts. Also the rates of deposition from them are slow so they cannot be used in modern high speed equipment. Moreover, they are corrosive.

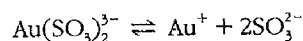
Apart from the chloride-free baths discussed above, other modern gold(III) baths are available commercially which do contain chloride but which contain substances which prevent formation of chlorine at the anode.

At present gold(III)/cobalt and gold(III)/nickel baths are used for plating stainless steel or chromium with flash coatings of gold (about 0.1 μm thick).

A gold(III)/indium bath has also been developed which yields deposits suitable for decorative applications on such substrates where an extremely light yellow colour is desired.

Sulphite Baths

Dissociation of the gold(I) sulphite complex occurs by the reaction:

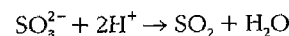
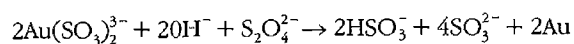
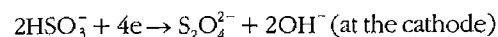
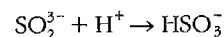


It is much less stable than the gold(I) cyanide complex and its stability constant is of the order of 10^{10} or about 10^{28} times less than that of the $\text{Au}(\text{CN})_2^-$ complex:

$$\frac{[\text{Au}(\text{SO}_3)_2^{3-}]}{[\text{Au}^+][\text{SO}_3^{2-}]^2} \approx 10^{10}$$

$$\text{and } [\text{Au}^+] \approx \frac{[\text{Au}(\text{SO}_3)_2^{3-}]}{[\text{SO}_3^{2-}]^2} \cdot 10^{-10}$$

However, at neutral and acid pH values the complex is unstable. Significant reactions which occur under these conditions are:



The formation of the dithionate ion $S_2O_4^{2-}$, which is a powerful reducing agent, leads to a gradual reduction of the gold complex to metallic gold (14). Below pH 4.7 the sulphite ion breaks down.

Reduction of the gold complex between pH 4.7 and 8.0 can be decreased considerably by strengthening the sulphite complex with ethylenediamine (16) or by adding an oxidising agent, like picric acid, that will react with the dithionate at a faster rate than the gold sulphite complex. However, the use of these additives makes the bath control difficult and is not completely effective.

Brighteners

Although brightness in itself is not important in gold plating for electronic applications, it is associated with other desirable qualities such as wear resistance and lack of porosity.

Brighteners for gold electrodeposits are of three types:

- Organic substances such as polyethyleneimines and high molecular weight polyamines. These operate by selective absorption within the Helmholtz double layer, usually causing an increase in polarisation. They are adsorbed onto the more prominent growth points so that the gold is deposited preferentially on other parts of the cathode surface, producing a levelling and brightening effect. Invariably the organic additive is incorporated into the structure of the deposit with adverse effects on its physical properties, especially wear resistance. The wear resistance can, however, be improved by co-depositing a second metal such as cadmium.
- Co-deposited metals and semi-metals such as arsenic, thallium, selenium, lead etc. The use of these causes depolarisation and they produce only lustrous deposits from cyanide baths but fully bright deposits from sulphite baths. They operate at extremely low concentrations of a few ppm and this has resulted in a number of theories as to how they work, but only one theory withstands examination. In this theory the semi-metals are regarded as being adsorbed evenly on the cathode surface where they catalytically enhance the nucleation of the gold. In the absence of these brighteners the gold nucleates at growth points such as crystal dislocations on the cathode, but the catalytic effect of the semi-metal encourages more even deposition by creating more growth points (17). The effect can be termed catalytic because the charged species, for example Tl^+ , is available for readsorption. The mechanism is even more efficient for sulphite golds.
- Co-deposited transitional metals such as cobalt, nickel and iron. For coatings used as contact materials on connectors and PCB's, these are the most important brighteners.

In describing the brightening action of transitional metals, cobalt can be taken as the example but the same arguments apply to some other metals. It has been known for some time that cobalt brightened gold deposits contain carbon (18,) in fact if a deposit does not contain at least 0.1 per cent carbon it will not be bright. C^{14} labelling techniques have shown that this carbon originates in the carbon of the cyanide ligand (19).

In some way the presence of cobalt is responsible for the creation of Munier's polymeric material in the gold deposit (2). Analysis has shown that as well as carbon these deposits also contain potassium, nitrogen and oxygen. It has been suggested (20) that a complex such as $KCo(Au(CN)_2)_3$ is formed and it is this material that acts as a brightener.

In a plating bath this complex is visualised as being formed within the Helmholtz double layer. Under the usual operating conditions it is only very slightly soluble, so that as it is formed it is adsorbed onto the cathode in an analogous manner to organic brighteners. Any parameter that increases the solubility of $KCo(Au(CN)_2)_3$, such as high pH or high temperature, would be expected to reduce its brightening effect. This is in accord with the fact that these transitional metals act as brighteners only in acid gold cyanide baths, whereas the semi-metals can brighten deposits from a much wider range of gold electrolytes. If this understanding is correct we should expect to find K, Co, C and N present in the brightened deposits in the same atomic proportions as those in which they are present in $KCo(Au(CN)_2)_3$, i.e. the atomic ratios of K:Co:C:N in acid gold deposits should be 1:1:6:6.

In practice these ratios can vary enormously, the K:Co varying from 1.0:0.4 to 1.0:5.5 depending on the electrolyte and the operating conditions (21). The Co:C ratio can vary from 1:3 to 1:10 (22). However, the atomic ratio of C:K is fairly constant at 3:1 (22), and the potassium in these deposits increases linearly with the electrolyte potassium concentration.

These results do not rule out $KCo(Au(CN)_2)_3$ as the main brightening agent but they strongly indicate that these elements are also present in other forms, for instance some workers have identified elemental cobalt, $CoOOH$ and cobalt cyanide in acid gold deposits (23,24).

Although the formation of $KCo(Au(CN)_2)_3$ is significant in that it explains many characteristics of the acid gold process, it may well be that this substance is only an important intermediate in the deposition process. It may be that other reactions contribute to the brightening process, namely the inclusion of potassium, the reduction and deposition of cobalt, and the formation of complex cyanides and polymers.

Table I

Typical Composition of an Acid Gold Deposit that is bright, has fairly low internal stress and is hardwearing

Element	% W/W	% Atom/Atom
K	0.26	1.3
C	0.24	3.94
Co	0.24	0.80
N	0.26	3.66
Total	1.00	9.70

A typical composition of an acid gold deposit that is bright, has fairly low internal stress and is hard wearing is given in Table I. These figures agree fairly well with those predicted by the $\text{KCo}(\text{Au}(\text{CN})_2)_3$ theory.

The presence in an acid gold plating bath of a strong ligand for cobalt can interfere with the formation of $\text{KCo}(\text{Au}(\text{CN})_2)_3$ and the brightening action, by removing cobalt ions from the system. Thus, if cobalt is added as the ethylenediamine tetraacetate complex, an overall cobalt concentration of about 6 g/l may be required to provide sufficient cobalt ions to allow the formation of $\text{KCo}(\text{Au}(\text{CN})_2)_3$.

There is, however, an extremely strong ligand in all acid gold cyanide baths, namely cyanide itself. The cyanocobaltate complex $\text{Co}(\text{CN})_6^{3-}$ is one of the most stable complexes known (4), so much so that when complexed to $\text{Co}(\text{III})$, cyanide ceases to be toxic. More significantly, when cobalt is complexed with cyanide it is no longer available to form $\text{KCo}(\text{Au}(\text{CN})_2)_3$. The formation of cyanocobaltate is encouraged by high $\text{Co}(\text{III})$ concentration and high free cyanide concentration.

In an acid gold system the free cyanide concentration is very low, as any free cyanide tends to form undissociated HCN , but at higher pH free cyanide concentrations are increased.

Therefore it is important, when baths are analysed for cobalt, that the analysis should differentiate between 'inert' and 'active' cobalt. Although the effect is not as strong when iron or nickel are used as brightening agents, it is nevertheless still operative in baths containing these brighteners.

As yet there is insufficient evidence to say conclusively what the state of the as-deposited cobalt is, but all observers are now agreed that there is non-metallic material present and that some, if not all, the cobalt is present in the form of a cyanide complex. However, the $\text{KCo}(\text{Au}(\text{CN})_2)_3$ theory does provide an explanation of the observed behaviour of cobalt-brightened acid gold baths.

Operating Parameters of Gold(I) Cyanide Baths

pH

pH influences the bath in a number of ways. High pH (~ 5.0) allows a higher concentration of free cyanide and therefore cyanocobaltate formation is greater. Also at higher pH the solubility of $\text{KCo}(\text{Au}(\text{CN})_2)_3$ increases so that its brightening ability is reduced. As mentioned earlier, chelates are used to control the supply of cobalt to the double layer and chelating strength is pH dependent. Finally, as the bath operates the pH will rise, and to counter this acid gold baths need to be well buffered. pH also affects efficiency in that the lower the pH, the higher the concentration of hydrogen ions; this favours deposition of hydrogen instead of gold.

Temperature

Increasing temperature increases the solubility of $\text{KCo}(\text{Au}(\text{CN})_2)_3$, and this leads to decreasing brightness. Chelating strengths are also temperature dependent. The effects of higher temperature can usually be corrected by increasing the gold and cobalt concentrations.

Barrel Plating

A barrel can act like a semi-permeable membrane by creating a separate catholyte within the barrel. Within the anolyte compartment the Co^{3+} concentration increases, whilst within the catholyte the pH and free cyanide increases. When the barrel is removed and allowed to drain, the two solutions mix and there is a rapid formation of cyanocobaltate. These effects can be countered by maintaining a low pH, increasing the flow of electrolyte through the barrel and by using the largest possible volume of electrolyte.

High Speed Plating

High speed acid gold solutions are designed to produce the same type of deposit as conventional vat plating. In order to do this it is usual to increase the gold and cobalt content so as to prevent local depletion around the cathode. For the same reason agitation in high speed plating becomes critical: jet plating is necessary to produce the required turbulence for very high current densities. Higher temperatures are needed to reinforce the effect of turbulence.

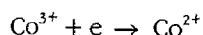
The main characteristics of high speed plating are the high anodic and cathodic current densities. Various effects result from this: the pH rises faster; more Co^{3+} is produced; conversion to cyanocobaltate is faster; and organic chelates tend to be anodically oxidised. As far as brightness alone is concerned, semi-metals are better additives at very high current densities.

Recently, a number of acid gold processes have been developed which make use of organic additives to increase the current density range of baths for deposition of cobalt and nickel brightened acid golds. This enables high speed plating to be done at lower concentrations than was previously possible.

Efficiency

By efficiency we mean that proportion of the applied current, usually expressed as a percentage, that results in the deposition of gold. The remaining current is responsible for the reduction of other species.

The reaction below is of little importance in terms of current consumption but the formation and adsorption of $\text{KCo}(\text{Au}(\text{CN})_2)_3$ increases the polarisation and thus encourages the deposition of hydrogen:



Any parameters that encourage the formation of $\text{KCo}(\text{Au}(\text{CN})_2)_3$, will therefore decrease the efficiency, for example low pH, high free cobalt concentration, low temperature.

The use of the correct chelating agents will control the availability of cobalt ions and thus the formation of $\text{KCo}(\text{Au}(\text{CN})_2)_3$ so that the best compromise between brightness and efficiency can be achieved.

Impurities

The effect of impurities can be exemplified by considering lead, which can act as a semi-metal brightener, but which in a cobalt acid gold bath inhibits the formation of $\text{KCo}(\text{Au}(\text{CN})_2)_3$. In the light of what has been discussed above about the catalytic effects produced in semi-metal brightening, it will be seen that lead could be expected to interfere with the formation of the brightener and cause depolarisation and an increase in efficiency. Most semi-metals interfere in this way, but Group 4 contaminants are more acceptable, at least in fairly low concentration.

Agitation

Compared with most base metal plating baths, precious metal baths have a low metal concentration in order to reduce inventory costs.

Nearly all the current in such baths is carried by the conducting salt, which is in relatively high concentration. The $\text{Au}(\text{CN})_2^-$ ion is not electrostatically attracted to the cathode and the supply of gold to the Helmholtz double layer is thus diffusion dependent. Agitation is therefore important as a means of increasing the supply of both gold and brightener to the cathode. This has both advantages and disadvantages in that high agitation can increase efficiency, but it also makes distribution worse by increasing the efficiency relatively more at high current densities than at low current densities.

Modern selective plating techniques have reduced the problems of metal distribution on the substrate and one of the other benefits of the new current density extending additives is that they also improve distribution.

Physical Properties of Deposits

The physical properties of gold deposits will now be considered in the light of the above.

Hardness

The hardness of a gold deposit is due to its structure or the impurities in the deposit or both. With acid cyanide deposits there is an almost direct relationship between hardness and base metal content, and it is possible to vary the hardness of a deposit by varying the chelate concentration in the electrolyte. With organically brightened golds the hardness increases with increasing brightener concentration, the causes of the increased hardness being higher impurity level and greater grain refining. The hardness of sulphite golds can be controlled by the amount of free brightener, usually arsenic, in the electrolyte but in this case the hardness is not due to arsenic in the deposit but to grain refining. It has now been realised that the relationship between hardness and wear resistance is not simple and straightforward, so that hardness is not regarded as being as important as it used to be.

Wear Resistance

Wear resistance is not a definite physical property but depends on very complex interactions of numerous factors. Hence, when comparing wear resistance it is important that the same experimental technique is used. Bright deposits have better wear resistance than dull deposits, acid gold bath deposits are better than organically brightened deposits, and these in turn have better wear properties than semi-metal brightened cyanide or sulphite golds. The cobalt brightened acid golds have a fine grained structure with a polymer framework which gives a tough deposit, whilst arsenic brightened sulphite deposits are very fine grained and almost amorphous; their fine grained structures being easily deformed. Organically brightened golds show acceptable wear resistance against themselves, but against the tough resilient deposits of an acid gold bath they are unacceptable.

More recent work (20) has indicated that the level of potassium has an important influence on the sliding wear resistance of acid gold deposits. However, as the atomic ratios of K:C and C:N in such gold deposits are fairly constant, it could be that the potassium level is only an indication of other features in the deposits which are responsible for their improved wear resistance.

Porosity

If the pre-treatment of the substrate is effective, the fine grained deposits from a semi-metal brightened deposit show less porosity than acid gold deposits. Unfortunately the deposit structure factors that reduce porosity tend to preclude other desirable properties.

The study of the formation of pores in acid gold deposits has made the formulation of low-porosity acid golds possible, but pretreatment still remains the most important factor in controlling porosity.

Stress

There are a number of theories that attempt to explain stress in electrodeposits; none of them are entirely satisfactory and only two will be considered.

The excess energy theory (23) states that an ion must pass an energy barrier in order to leave its ligand field and become an atom in a solid lattice. This additional energy barrier is responsible for polarisation. Once over this energy barrier, the atom will have excess energy which is converted into heat so that each freshly deposited layer is hotter than the rest of the solid. On cooling this gives rise to tensile stress. The relatively high stress in acid golds and the low stress in sulphite golds is explained in this way. On this basis, however organically brightened gold should be high in tensile stress and this is not necessarily so.

The dislocation theory (24,25) states that impurities cause extra dislocations in the metal lattice, which cause stress in acid golds and sulphite golds. In terms of this theory certain organics should give rise to compressive stress because they disguise some of the surface vacancies which lead to dislocations.

It is known from empirical observations that a deposit containing more than 0.3 per cent w/w Co or Ni will probably be too highly stressed, and this would fit in with the second theory.

Stress is probably generated in more than one way and it is unlikely, therefore, that one theory will ever supply all the answers.

Acknowledgement: This paper incorporates contents from an earlier publication (3) by the author. They are reproduced with the permission of the Institute of Metal Finishing.

Table II	
Densities of Acid Gold Deposits	
Electrolyte	Density (g/cm ³)
Low efficiency, cobalt brightened	17.30
Low efficiency, nickel brightened	16.62
High efficiency, cobalt brightened	16.40
High efficiency, nickel brightened	16.62
Pure gold	19.30

Density

Table II shows the densities of acid gold deposits. The figure for pure gold deposit is included.

The much lower density of cobalt and nickel brightened acid gold deposits cannot be explained on the simple assumption that the deposit contains 0.2 per cent cobalt or nickel. For the density to have fallen so much, the structure of the gold deposit must have been expanded by the inclusion of relatively light weight material.

It has been indicated above that in acid gold deposits up to 10 per cent of the atoms are not gold but are much lighter elements. This explains their lower density.

Conclusion

The early acid gold processes were developed empirically and it is only in the past few years that the relationship between the composition and operating parameters of the electrolyte, and the composition and performance of the deposits have begun to be understood. If significant advances are to be achieved, a more rigorous theoretical basis is required as a guide in exploring avenues of future development. □

References

- 1 J. Souter, *Trans. I.E.E.E.* Part 1, Hybrid Pack, March 1974, 18
- 2 G.B. Munier, *Plating*, 1969, **56**, 1151-1157
- 3 P. Wilkinson, *Trans. Inst. Met. Finish.*, 1981, **59**, 57-60
- 4 'Stability Constants', *Chem. Soc.*, Special Publication No. 17, 1964, 111 and 109
- 5 A. Knödler, *Metaloberfläche*, 1979, **33**, 7
- 6 Y. Okinaka, *West. Elect. Eng.*, 1978, **22**, (2), 72-81
- 7 E. Freedman and J.N. Shea, *U.S. Pat.* 3598706, 1971
- 8 A. Fletcher and W.L. Moriarty, *U.S. Pat.* 4168214, 1979
- 9 Oxy Metal Industries, *German Pat.* DE-OS 2658003, 1976
- 10 W. Zilske, *German Pat.* DE-OS 3012999 A1, 1981
- 11 J.M. Deuber and H.J. Luebke, '72nd Ann. Tech. Conf. Proc., Am. Electroplaters' Soc.', 1985, G3
- 12 Arakawa Kako KK, *Jpn. Pat. Appl.* 57174487, 1981
- 13 Arakawa Kako KK, *Jpn. Pat. Appl.* 57203787, 1981
- 14 Arakawa Kako KK, *Jpn. Pat. Appl.* 57203788, 1981
- 15 J.P. Derivaz, A. Resin and S. Losi, *Surf. Technol.*, 1977, **5**, 369-377
- 16 S.A. Losi, F.L. Zuntini and R.A. Myer, *Electrodeposition Surf. Treatment*, 1972/1973, **1**, 3-19; *Surfaces* (Paris), 1973, **12**, 67-75
- 17 S.T. Rao and R. Weil, *Trans. Inst. Met. Finish.*, 1979, **57**, 97-101
- 18 D.R. Mason and A. Blair, *Trans. Inst. Met. Finish.*, 1972, **50**, 138-140
- 19 L. Holt and J. Stanyer, *Trans. Inst. Met. Finish.*, 1972, **50**, 24-27
- 20 E.T. Eisenmann, *J. Electrochem. Soc.*, 1977, **124**, 1957-1958
- 21 J. Souter *et al.*, 'Connectors '85, Leicester', 1985, 43
- 22 P. Wilkinson and C. Martin, 'ICT Conf. Brunel University', 1984
- 23 H. Leidheiser *et al.*, *J. Electrochem. Soc.*, 1979, **126**, 391-394
- 24 R.L. Cohen *et al.*, *J. Electrochem. Soc.*, 1979, **126**, 1608-1618
- 25 Ya.M. Popeneka, *Fiz. Met. Metalloved.*, 1965, **20**, (5), 753